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STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXII. The Rotatory Dispersion of Enantiomeric *o*-, *m*-, and *p*-Nitrobenzalaminomethylenecamphors and *p*-Dimethylaminobenzal-aminomethylenecamphors

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IN this paper, we present experimental data on the rotatory dispersion of the condensation products of aminomethylenecamphor (*d*, *l* and *dl*) with *o*-, *m*- and *p*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde. The condensation products from benzaldehyde were oils which refused to solidify.

The Influence of Chemical Constitution on the Rotatory Power.—Mario Betti[1] studied the effect of chemical constitution on rotatory power in compounds of the type, $C_6H_5-\underset{\displaystyle C_{10}H_6(OH)\beta}{\overset{\displaystyle H}{\underset{|}{C}}}-N=CHR$, by condensing the optically active, β-naphtholbenzylamine and aldehydes. The molecular rotatory power, $[M]_D$, of the compounds varied from $+2676°$ to $-991°$, and when it was arranged in order of magnitude, it gave a series which agrees, subject to minor variations, with that representing the dissociation constants (K) of the acids, derived from the aldehydes employed (Table A) :—

TABLE A

$[M]_D$ of the derived compound	Aldehyde	$K \times 10^5$ for derived acid
2676°	*para*-dimethylaminobenzaldehyde	1 (?)
1507	veratric aldehyde	3·6
1250	anisaldehyde	3·2
1220	vanillin	3·0
1049	*para*-hydroxybenzaldehyde	2·9
894	*ortho*-methoxybenzaldehyde	8·2
+746	cuminic aldehyde	5·0
373	benzaldehyde	6·0
363	*meta*-hydroxybenzaldehyde	8·7
207	*para*-nitrobenzaldehyde	39·4
168	*meta*-nitrobenzaldehyde	34·5
− 991	*ortho*-nitrobenzaldehyde	616·0

Berlingozzi[2] also obtained approximately similar results with derivatives of asparagine.

Our values of rotatory power of derivatives of benzalaminomethylene-camphor in different solvents together with those of K, the dissociation constant are given in Table B :—

TABLE B

Structural formula	Methyl alcohol	Ethyl alcohol	Acetone	Chloroform	Pyridine	$K \times 10^5$ for derived acid
I. *R·N = CH–C$_6$H$_4$–NO_2 (o) ..	319·7° (65·66)	301·9° (63·97)	305·6° (64·7)	304·7° (58·32)	261·5° (57·12)	616
II. R·N = CH–C$_6$H$_4$–NO_2 (m) ..	325·0 (66·03)	313·3 (61·14)	303·9 (61·01)	300·8 (60·62)	281·0 (53·5)	34
III. R·N = CH–C$_6$H$_4$–NO_2 (p) ..	335·0 (66·64)	326·2 (65·2)	318·1 (61·3)	321·9 (63·5)	292·0 (53·5)	39·6
IV. R·N = CH–C$_6$H$_4$–$N(CH_3)_2$ (p)	188·2 (42·81)	187·8 (40·4)	172·4 (34·5)	167·2 (32·01)	..	11

* R = C_8H_{14} (C = CH—, C = O)

Whereas the order of rotatory power of Betti's compounds, and the dissociation constant (K) of the substituted benzoic acids corresponding to the aldehydes employed are

$$[M]_D: \; p - N(CH_3)_2 > p - NO_2 > m - NO_2 > o - NO_2,$$

$$K: \quad p - N(CH_3)_2 < p - NO_2 < m - NO_2 < o - NO_2;$$

these sequences in the case of similar derivatives of benzalaminomethylene-camphor are

$$[M]_{5460}: p - N(CH_3)_2 < o - NO_2 < m - NO_2 < p - NO_2,$$

$$K: \quad p - N(CH_3)_2 < p - NO_2 < m - NO_2 < o - NO_2.$$

The above mentioned parallelism between the rotatory power and the dissociation constant, which is complete in Betti's compounds, holds only partially in the case of our compounds. The causes of the disparity between these two results seem to be two : (*a*) whereas there is only one asymmetric

carbon atom in the molecule of benzal derivatives of β-naphthol benzylamine, $C_6H_5-\underset{\underset{C_{10}H_6(OH)\beta}{|}}{\overset{\overset{H}{|}}{C}}-N=CHR$, which is relatively of simple structure, there are two asymmetric carbon atoms in the molecule of derivatives of benzalaminomethylenecamphor,

$$\begin{array}{l} CH_2-\overset{\overset{H}{|}}{C}- \quad\quad C=CH\cdot N=CH\cdot R \\ \quad\quad\quad\

TABLE I

Ortho-*Nitrobenzalaminomethylenecamphors*

Solvent	Ethyl alcohol		Methyl alcohol		Pyridine		Chloroform		Acetone	
Concentration g./100 c.c.	*d* 0·4000	*l* 0·4008	0·4000	0·4008	0·4016	0·4008	0·4004	0·4012	0·3600	0·3772
Calculated [α]	$\pm \frac{63\cdot97}{\lambda^2-0\cdot0860}$		$\pm \frac{65\cdot66}{\lambda^2-0\cdot0928}$		$\pm \frac{57\cdot12}{\lambda^2-0\cdot0786}$		$\pm \frac{58\cdot32}{\lambda^2-0\cdot1070}$		$\pm \frac{64\cdot70}{\lambda^2-0\cdot0862}$	
Calculated λ_0	0·2934		0·3047		0·2804		0·3272		0·2936	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5085}	+370·6°	−368·8°	+395·9°	−394·3°	+317·4°	−316·9°	+384·8°	−384·0°	+375·3°	−374·
Ag_{5209}	344·3	343·7	368·4	365·6	296·3	295·7	353·5	354·0	..	..
Hg_{5460}	301·9	301·2	319·7	319·2	261·5	261·3	304·7	305·4	305·6	304·
Hg_{5780}	258·3	256·3	273·4	273·2	224·1	223·4	258·4	258·0	261·2	260·
Na_{5892}	247·0	243·8	257·5	256·8	212·4	213·4	242·3	244·4	248·6	248·
Li_{6103}	223·4	221·3	233·5	233·3	195·5	196·2	218·5	218·8	226·4	227·
Cd_{6438}	197·2	195·4	204·2	204·4	..	..	188·4	188·2	197·2	196·
Li_{6708}	176·0	175·0	183·1	183·6	156·2	152·3	169·8	168·3	177·8	178·
	No mutarotation				No mutarotation		No mutarotation			

TABLE II

Meta-*Nitrobenzalaminomethylenecamphor*

Solvent	Ethyl alcohol		Methyl alcohol		Pyridine		Chloroform		Acetone	
Concentration g./100 c.c.	*d* 0·4040	*l* 0·4044	0·4056	0·4040	0·4024	0·4016	0·4056	0·4040	0·4048	0·4044
Calculated [α]	$\pm \frac{61\cdot14}{\lambda^2-0\cdot1023}$		$\pm \frac{66\cdot03}{\lambda^2-0\cdot0946}$		$\pm \frac{50\cdot62}{\lambda^2-0\cdot1178}$		$\pm \frac{53\cdot50}{\lambda^2-0\cdot1196}$		$\pm \frac{61\cdot01}{\lambda^2-0\cdot0975}$	
Calculated λ_0	0·3199		0·3077		0·3433		0·3459		0·3123	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5085}	+391·1°	−390·9°	+403·6°	−404·0°	+358·7°	−359·3°	+384·7°	−383·4°	+380·5°	−378·
Ag_{5209}	363·8	361·1	374·8	375·0	330·6	331·2	351·1	350·3	351·0	350·
Hg_{5460}	313·3	311·6	325·0	323·4	281·0	282·6	300·8	300·8	303·9	305·
Hg_{5780}	263·3	263·3	275·0	274·6	234·1	234·6	250·3	250·0	257·0	258·
Na_{5892}	248·5	248·5	261·3	260·4	221·3	220·4	234·2	235·1	244·6	244·
Li_{6103}	226·5	225·1	238·9	239·0	200·1	198·0	210·9	212·9	223·6	222·
Cd_{6438}	195·6	196·9	205·9	206·5	170·3	168·1	180·0	180·7	192·7	191·
Li_{6708}	175·7	176·8	185·0	186·0	152·9	151·6	160·3	159·6	173·0	171·
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE III

Para-*Nitrobenzalaminomethylenecamphor*

Solvent	Ethyl alcohol		Methyl alcohol		Pyridine		Chloroform		Acetone	
Concentration g./100 c.c.	*d* 0·4016 *l* 0·4040		0·4004 0·4000		0·4008 0·4004		0·4040 0·4032		0·4024 0·4016	
Calculated [α]	$\pm \frac{65{\cdot}20}{\sqrt{\lambda^2 - 0{\cdot}0976}}$		$\pm \frac{66{\cdot}64}{\sqrt{\lambda^2 - 0{\cdot}0992}}$		$\pm \frac{53{\cdot}80}{\sqrt{\lambda^2 - 0{\cdot}1140}}$		$\pm \frac{63{\cdot}50}{\sqrt{\lambda^2 - 0{\cdot}1010}}$		$\pm \frac{61{\cdot}30}{\sqrt{\lambda^2 - 0{\cdot}1056}}$	
λ_0	0·3125		0·3152		0·3376		0·3178		0·3250	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5085}	+404·6°	−403·5°	+417·5°	−418·4°	+373·2°	−373·0°	+402·3°	−403·1°	+401·5°	−400·7°
Ag_{5209}	374·8	376·3	387·5	387·0	342·0	341·2	..	..	370·5	372·2
Hg_{5460}	326·2	326·8	335·0	334·8	292·0	291·1	321·9	323·0	318·2	318·0
Hg_{5780}	275·1	275·0	283·7	282·6	245·9	244·9	273·5	272·7	268·4	266·8
Na_{5892}	261·5	262·4	269·3	268·4	230·9	232·0	257·5	257·6	254·8	254·0
Li_{6103}	237·8	237·0	243·1	244·1	208·4	207·5	234·0	235·3	228·7	227·7
Cd_{6438}	204·2	204·0	211·1	212·0	178·4	178·7	201·7	200·8	200·3	199·7
Li_{6708}	184·3	185·6	190·9	189·7	156·0	155·1	181·9	180·9	177·8	177·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No Mutarotation	

TABLE IV

Para-*Dimethylamidobenzalaminomethylenecamphor*

Solvent	Ethyl alcohol		Methyl alcohol		Chloroform		Acetone	
Concentration g./100 c.c.	*d* 0·4044 *l* 0·4044		0·4020 0·4016		0·4020 0·4032		0·4008 0·4012	
Calculated [α]	$\pm \frac{40{\cdot}40}{\sqrt{\lambda^2 - 0{\cdot}0822}}$		$\pm \frac{42{\cdot}81}{\sqrt{\lambda^2 - 0{\cdot}0726}}$		$\pm \frac{32{\cdot}01}{\sqrt{\lambda^2 - 0{\cdot}1060}}$		$\pm \frac{34{\cdot}60}{\sqrt{\lambda^2 - 0{\cdot}0945}}$	
λ_0	0·2868		0·2694		0·3256		0·3075	
Line	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5085}	+229·0°	−229·0°	+230·1°	−229·8°	+209·7°	−209·7°	+210·9°	−211·7°
Ag_{5209}	214·0	212·7	216·4	214·1	194·2	193·4	197·1	195·7
Hg_{5460}	187·9	187·9	188·2	190·4	167·2	165·7	172·4	172·0
Hg_{5780}	160·7	162·9	161·8	163·1	140·8	139·7	146·7	145·2
Na_{5892}	152·1	153·3	155·5	156·8	132·9	133·5	139·2	139·5
Li_{6103}	139·7	141·0	141·9	140·8	121·4	121·4	119·8	120·2
Cd_{6438}	121·2	120·0	125·4	125·5	106·2	106·9	110·7	110·9
Li_{6708}	110·1	107·8	113·2	112·1	93·04	93·10	97·32	97·80
	No mutarotation		No mutarotation		No mutarotation		No mutarotation	

systematic errors. For the sake of economy of space, the values of differences ($o - c$) are omitted from the tables. In the case of these compounds, which exhibit simple dispersion, the effects of dispersion can be eliminated by using the rotation constant, k_0, of the one-term equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$, as a measure of the optical rotatory power of the medium. This value of rotation (k_0) is for a wavelength λ, not very much larger than 10,000 Å·U at which $\lambda^2 - \lambda_0^2 = 1$ square-micron. These values of the rotation constant (k_0) are given in brackets in Table B, and are found on comparison to lead to similar conclusions as regards the effect of solvent, position isomerism and other factors on rotatory power.

The physical identity of enantiomorphs.—The values of the rotatory power of the *d*- and *l*-forms in different solvents (Tables I to IV) are identical within the limits of experimental error. Out of about 150 observations which are now recorded, in as many as 125 cases, this difference in the numerical value of the rotatory power of the opposite isomers corresponds to a difference of less than 0°·01 in the observed angle of rotation and in other 24 cases, the corresponding angle lies between 0°·01 and 0°·02, which is the limit of experimental error allowable in such measurements. Only in the case of *o*-nitrobenzalaminomethylenecamphor in pyridine for Li $_{6\,7\,0\,8}$ (Table I), the difference corresponds to 0°·03 in the observed angle of rotation. This, therefore, further supports Pasteur's principle of molecular dissymmetry according to which the two forms, dextro and lævo, must possess equal and opposite rotatory power.

The nature of the racemic modification can be generally inferred from the melting points of the optically active and racemic forms :—

(i) the melting point of the racemic forms of *o*-, and *p*-nitrobenzalaminomethylenecamphor are higher than those of the optically active isomers ; they are, therefore, true *dl*-compounds, at least in the solid state.

(ii) the melting point of the racemic form may be identical with that of the optically active modification as in the case of *p*-dimethylaminobenzalaminomethylenecamphor; the racemic form in this case also is a *dl*-compound.

(iii) the melting point of the racemic form may be lower than that of the optically active variety as in the case of *m*-nitrobenzal aminomethylenecamphor: the racemic form may be a mixture (conglomerate) or a compound. In order to decide this point, melting point-composition curves of the optically active forms with the racemic modification will have to be prepared. The same method will have to be employed

also in distinguishing a racemic solid solution from the other two. The diagram for a racemic solid solution will consist of one curve, for a mixture of two curves and for a compound of three curves.

Experimental

o-Nitrobenzalaminomethylene-d-camphor (Formula I, Table B).—Aminomethylene-*d*-camphor (1 mol. proportion) dissolved in methyl alcohol was added to *o*-nitrobenzaldehyde (1 mol. proportion) and was heated at 45–50° C. for about three hours, when a heavy oily liquid was obtained. If the temperature is raised above this point, the aminomethylenecamphor changes into iminomethylenecamphor with loss of ammonia, and no condensation can then be effected. The oily product on keeping under water for two days solidified and was crystallised from aqueous methyl alcohol as yellowish needles, melting at 168–170°. The yield was rather poor. It is soluble in chloroform, ether, acetone, pyridine, ethyl and methyl alcohol, and sparingly soluble in benzene. The *lævo* (m.p. 168–170°) and racemic forms (m.p. 182–183°) were obtained in the same way and had similar solubility.

Found : *Dextro* (C, 68·90 ; H, 6·60 ; N, 9·77 per cent.) ; *Lævo* (N, 9·03 per cent.) ; Racemic (N, 9·06 per cent.).

m-*Nitrobenzalaminomethylenecamphors* (Formula II, Table B).—These were prepared in the same way as the *ortho* isomerides, except that the time of heating was 5 hours.

Dextro : yellowish needles, from a red heavy oily liquid ; crystallised from aqueous ethyl alcohol as yellowish needles, m.p. 159–161°.

Found : C, 68·90 ; H, 6·80 ; N = 9·01 per cent.

The *lævo* and racemic modifications had similar properties as the *dextro* isomeride.

Lævo : m.p. 159–161° ; N, 8·99 per cent.

Racemic : m.p. 150–152° ; N, 8·97 per cent.

p-*Nitrobenzalaminomethylenecamphors* (Formula III, Table B).—These compounds were very difficult to prepare. The aldehyde and the base together with some anhydrous sodium sulphate in the presence of methyl alcohol were heated at 45–50° on the water bath for 12 hours. A deep red heavy oily liquid was obtained which on being kept under water for a week solidified. It was crystallised from aqueous methyl alcohol (charcoal) as a microcrystalline powder.

Dextro : m.p. 200–202° C. ; C, 68·90 ; H, 6·80; N, 9·01 per cent.

Lævo : m.p. 200–202° C. ; N, 8·99 per cent.

Racemic : m.p. 214–216° C ; N, 8·97 per cent.

$C_{18}H_{20}O_3N_2$ requires C, 69·23 ; H, 6·40 ; N, 8·97 per cent.

p-*Dimethylaminobenzalaminomethylenecamphors* (Formula IV, Table B).—The three isomers were prepared by mixing equimolecular proportions of *p*-dimethylaminobenzaldehyde and the corresponding base with a little anhydrous sodium sulphate in methyl alcoholic solution in the cold. The mixture was kept for an hour and then poured into water when a yellowish solid separated. It was crystallised from aqueous methyl alcohol (charcoal) as yellowish needles. All the three isomers melt at 66–68°.

Found : *Dextro* : C, 77·30 ; H, 8·91 ; N, 9·23 per cent.

Lævo : N, 9·28 per cent.

Racemic : N, 9·24 per cent.

$C_{20}H_{26}ON_2$ requires C, 77·41 ; H, 8·38 ; N, 9·03 per cent.

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35° C. The value of the dispersion constant λ_0, calculated from the dispersion formula, is given in Tables I to IV and is expressed as μ or 10^{-4} cm.

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ON DISJUNCTION IN INTUITIONIST LOGIC

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§ 1. The Intuitionist approach to Mathematics differs from the classical approach in two fundamental respects[1]; namely,

(A) it insists on a constructive interpretation of all existential propositions;

(B) it discards the Principle of Excluded Middle, namely the assertion that a mathematical proposition must be either true or false.

It becomes evident from intuitionist reasoning that these two features (A) and (B) are interdependent and must be taken together.

From Heyting's formalisation of intuitionist logic it is seen that the set P of all propositions constitutes a *Brouwerian lattice*, that is, a distributive lattice with 0, 1, in which every element has a product-complement relative to every other. The lattice-product $a \cdot b$ of two elements a, b of P is their *conjunction*, namely the proposition '*a and b*'; the lattice-sum $a \oplus b$ of the propositions a, b is their (intuitionist) *disjunction*, namely the proposition '*a or b*'. The absolute product-complement a' of a in the Brouwerian lattice P is its (intuitionist) *negation not-a*, while the product-complement of a relative to b is the (intuitionist) implication $a \supset b$[2]. This implication is the ordering relation of P, so that any element of P represents a whole class of intuitionistically equivalent propositions; in particular, the elements 0, 1 of P stand for the class of false and true propositions respectively. In classical logic, P contains only the two elements 0, 1, since, according to the Principle of Excluded Middle, any proposition must be either true or false, so that it is equivalent to 1 or to 0. Thus, the significance of (B) is, that the (intuitionist) propositional lattice P contains elements other than 0 and 1.

§ 2. *Classical and Intuitionist Disjunction*

An existential proposition is of the form

$$(Ex)\ F(x)\ \{\text{or } E(x, y, \cdots)\ F(x, y, \cdots)\}$$

where x is an object-variable with assigned range, and F is a predicate. According to (A) this must be interpreted constructively; that is, $(Ex)\ F(x)$

means that a systematic process is available for constructing an x from the range, with the predicate F. An existential quantor thus interpreted may be called *strong*, and written with double brackets $\{((Ex))\ F(x)\}$.

But an existential proposition $(Ex)\ F(x)$ can be viewed as a finite or infinite disjunction of propositions of the form $F(x_i)$. Hence the constructive interpretation demanded in (A) must be carried over to intuitionist disjunction $\oplus$. Thus, if a, b are two propositions, the assertion of $a \oplus b$ must mean 'one of the propositions a, b is true, and a systematic process can be produced for determining which of them is true'. This (intuitionist) disjunction may be called '*strong disjunction*'. The strong disjunction is the lattice-sum in P, and therefore distributes, and is distributed by, 'conjunction' (*i.e.*, the connective *and*).

But the usual or classical disjunction, which we may denote by $+$, occurs in our ordinary thought-process and reasoning, and must be accepted in some form as an operation in the lattice P. We must however make a choice from among its meanings, which though mutually equivalent in classical logic, become distinct in Intuitionist logic, when we discard the principle of the excluded middle. We accordingly define *weak disjunction** as follows, and denote it by $+$:

DEF.: *The weak disjunction* a + b *of two propositions* a, b *is defined to mean the impossibility of the simultaneous falsity of* a *and* b.

Analogously, the weak existential quantor (Ex) may be defined, by prescribing $(Ex)\ F(x)$ to mean the impossibility of $F(x)$ being false for all objects x.

It is clear from the definition that the strong disjunction $a \oplus b$ implies the corresponding weak disjunction $a + b$, and also that the strongly quantised proposition $((Ex))\ F(x)$ implies the corresponding weakly quantised proposition $(Ex)\ F(x)$. It is also clear that weak disjunction is commutative and associative, but the interesting point is that *it is not tautological.* For, $a + a = a'' \pm a$, since the principle of excluded middle is not accepted. The precise relation between strong and weak disjunction is given by:

THEOREM I: *The weak disjunction is the double negation of the corresponding strong disjunction; the weakly quantised proposition* $(Ex)\ F(x)$ *is the double negation of the corresponding strongly quantised proposition.*

* Propositions may be described as relatively strong or weak, according to the size of their set of implications. Thus a is stronger than b if and only if every proposition implied by b is also implied by a, that is, if and only if, a implies b. This description may naturally be carried over to operations like disjunction.

For, from the definition $a+b=(a'\ b')'=(a \oplus b)''$; and $(Ex)\ F(x)=$ not $-\{(x)$ not $-F(x)\}=\{((Ex))\ F(x)\}''$.

It follows that the weak disjunction $a+b$ is the *normalised sum* of a and b in P. Now the negative propositions (or normal elements) of P form a boolean algebra N in which the boolean product is the same as conjunction, and the boolean sum is the normalised sum. Thus the boolean operations in N are conjunction and weak disjunction. Hence:

THEOREM II: *So long as we are dealing only with negative propositions, weak disjunction is tautological, and stands in the relation of mutual distributivity to conjunction.*

More generally the formal relations of conjunction and weak disjunction in P are given by :

THEOREM III: *Conjunction distributes weak disjunction; conjunction with a proposition* c *is distributed by weak disjunction if* c *is a negative proposition.*

For, if x, y are elements of P, $(xy)''=(x'+y')'''=(x'+y')'=x''y''$.

Hence

$a+bc=\{a \oplus bc\}''=\{(a \oplus b)(a \oplus c)\}''=(a \oplus b)''\cdot(a \oplus c)''=(a+b)(a+c)$.

Further, $ca+cb=\{ca \oplus cb\}''=\{c(a \oplus b)\}''=c''\cdot(a \oplus b)''=c''(a+b)$.

Hence $c(a+b)=ca+cb$ if and only if $ct=c''t$, where $t=a+b$. Now t is a negative proposition, and therefore $ct=c''t=c''t''=(ct)''$ if and only if ct is a negative proposition. This will be true if c is a negative proposition (since t is a negative proposition by Theorem I).

§ 3. *The Principle of Excluded Middle*

In intuitionism the falsity of a proposition a is interpreted positively, namely, as *the capacity of* a *to imply a contradiction.* Hence we must distinguish between a merely failing to be true, and a being false. In the lattice P, the relations $a=1$, $a \neq 1$, $a=0$ express respectively that a is true, a is not true, and a is false.

THEOREM IV: *The truth and the falsity of* a *are both operations in P; the untruth of* a *is* not *however an operation in P.*

For the truth of a is the proposition $a=1$, which cannot be distinguished from a itself, since asserting a is the same as asserting the truth of a; hence it is the identical operation in P. The falsity of a is the proposition $a=0$, or the (intuitionist) negation of a; it is the product-complement a' of a in P, and hence an operation in P. But the untruth of a is the proposition $a \neq 1$; this cannot be an element of P, since negation occurs here in the classical

sense which satisfies the principle of excluded middle. In the same way, if a, b are elements of P, 'a implies b' is also an element of P, namely the product-complement of a relative to b; but 'a does not imply b' is not a member of P, though the proposition 'it is false that a implies b' is a member of P.

In the principle of excluded middle in (B), the disjunction 'or' occurs; the principle itself may be called 'the *strong* or the *weak* principle of excluded middle', according as the disjunction is interpreted as strong or weak disjunction. It is clear in the first place that the weak principle of excluded middle is true in intuitionist logic, and cannot be rejected; for obviously, if a is any proposition, it is false that both a and not-a can be simultaneously false. Hence it is the strong principle of excluded middle that is rejected. The rejection of course does not amount to assertion of the falsity of the principle. A more precise recognition of the status of the principle of excluded middle is contained in Brouwer's dictum of *the absurdity of the absurdity of the principle of excluded middle* [which corresponds to the lattice-property $(a \oplus a')' = 0$, for any a in P]. A proposition in P whose absurdity is absurd, may be called *half-true*.[3] The half-true propositions are the elements of P whose product-complement is 0, and they therefore constitute the ideal Π_α* of P. Brouwer's dictum amounts therefore to the half-truth of the principle of excluded middle. It may be noted also that any half-true proposition a has the form of a disjunction $b \oplus b'$; for, since a is half-true, $a' = 0$ and therefore $a = a \oplus a'$.

§ 4. *Other Meanings of Disjunction Equivalent to Classical Disjunction*

The weak disjunction $a + b$ (defined as the falsity of the simultaneous falsity of a, b) is the only equivalent of classical disjunction which can be represented within the Intuitionist system. The two other equivalents which can be obtained by replacing 'falsity' by 'untruth' in either of its occurrences in the definition of weak disjunction, cannot, by Theorem IV, be regarded as operations in P, since they involve the notion of 'untruth'.† They are however significant as operations in the metalogic of the Intuitionist system. They are as follows:

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* The ideals Π_α, Π_μ of a general distributive lattice with 0, 1 were introduced by the author in the recent paper 'On the lattice of open sets of a topological space', *Proc. Ind. Acad. Sci.*, December 1942.

† If X is a metalogical proposition not representable in the system, we cannot distinguish between 'X is untrue' and 'X is false', since the metalogic is classical, and obeys the principle of excluded middle. Taking $X =$ 'a and b are both untrue', it follows that the proposition 'it is untrue that both a and b are untrue' cannot be distinguished from the intermediate disjunction $a +_1 b$. Hence there are only *two* (not three) other equivalents of classical disjunction.

(1) Intermediate disjunction $a +_1 b$, meaning 'it is false that both a and b are untrue' or equivalently 'an unspecifiable one of a, b is true'.

(2) Weaker disjunction $a +_2 b$, meaning 'it is untrue that both a and b are false', or equivalently 'at least one of a, b is not false'. It is clear that the strong disjunction $a \oplus b$ implies the intermediate disjunction $a +_1 b$, which implies the weak disjunction $a + b$, which again implies the weaker disjunction $a +_2 b$. The reverse implications do not hold.

Considering the principle of excluded middle as a primarily metalogical one, which may or may not be representable within the formalism of the system, we may examine the *intermediate* and *weaker* principles of excluded middle which arise when the disjunction therein is interpreted as intermediate or weaker disjunction respectively. It is clear that the weaker principle of excluded middle is valid, since it is implied by the weak principle of excluded middle which was seen to be valid in intuitionist logic. On the other hand the intermediate principle of excluded middle, stating that one of the alternatives a or *not-a* is always true, is clearly not valid and must be rejected in intuitionist logic. Since the strong principle of excluded middle implies the intermediate principle, the rejection of the former may be viewed as a consequence of the rejection of the latter.

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HYSTERESIS IN SORPTION—X

Open Pore Volume in Relation to Particle Radius

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Introduction

To explain the interesting phenomenon of Drift with other changes of the hysteresis loop[1] in the sorption of water on ferric oxide gel, a theory of the coalescence of the particles of the porous system accompanying successive sorption and desorption has been advanced. In support of the theory a mathematical formulation has been made which relates the cavity volume with particle radius in a system of closely packed spherical particles of equi-radius. The formula indicates that mass remaining the same, the total cavity volume decreases as particle radius increases. The total capillary volume in such a system however is made up of cavities as well as open pores. Calculation of the open pore volume and its relation with particle radius[2] which were omitted in the previous communication (*loc. cit.*) are presented in this paper.

An Open Pore

By placing four spherical particles in juxtaposition, a cavity and four adjacent open pores are formed. Let all the four spherical particles be of the same radius r. The centres of these four spherical particles lie at the vertices of a regular tetrahedron of edge $2r$. The cavity will have four necks which lie in the four faces of the tetrahedron. In continuation of these necks there are the four open pores surrounding the cavity. Such an open pore has a tapering from one end which is wide to the other end which is narrow. In order to calculate the volume of each open pore it is necessary to specify its boundaries. The central part of the open pore is made up of portions of surfaces of the three spheres forming the open pore. On the side where it adjoins the cavity, the open pore ends in the plane of the neck of the cavity and on the opposite side in the plane tangential to the three spheres forming the open pore. The boundary between two adjoining open pores remains to be specified. When all the open pores are completely filled with a liquid, the liquid meniscus in any open pore will be a triangular plane surface (part of the tangential plane above referred to) ending at the three edges with

portions of a cylindrical surface. Every open pore has, in this way, its boundary at the wide end made up of a triangular plane and three bits of a cylindrical surface at the edges.

The Volume of an Open Pore

The volume of an open pore is therefore made up of two parts, (1) the volume V_1 bounded by the triangular part of the meniscus, the plane of the neck and the surfaces of the spheres. (2) The volume $3\,V_2$ included berween the spheres and the cylindrical parts of the meniscus.

The volume V_1 is the difference between the volume of the right prism obtained by drawing perpendiculars on the common tangent plane (triangular part of the meniscus) from the centres of the three spheres and the volume of the portions of these spheres, lying inside the prism. Hence $V_1 = \left(\sqrt{3} - \frac{\pi}{3}\right) r^3$.

Let V_2 be the volume included between the cylindrical part of the meniscus and the spheres. Of the three such cylindrical parts each is a part of the surface of a complete cylinder of length $2r$ and radius r and the volume included between this cylindrical surface and the surfaces of the two hemispheres which are enveloped by the cylinder $= \frac{2}{3}\pi r^3$. If 2α is the angle between the planes of the wide ends of two adjoining open pores, $V_2 = \frac{\alpha}{2\pi} \cdot \frac{2}{3}\pi r^3 = \frac{1}{3}\alpha r^3$. But 2α is also the angle between two adjacent faces of the tetrahedron. Therefore $\alpha = \frac{1}{2}\cos^{-1}\frac{1}{3}$ and $V_2 = \frac{1}{6}\left(\cos^{-1}\frac{1}{3}\right) r^3$.

There are three such cylindrical portions in each open pore. Hence the volume of an open pore

$$= V_1 + 3\,V_2 = \left(\sqrt{3} - \frac{\pi}{3} + \frac{1}{2}\cos^{-1}\frac{1}{3}\right) r^3.$$

Total Open Pore Volume

The total number of open pores when there are N spherical particles is to be calculated. At least three spheres are required for the formation of an open pore and by placing them in close contact two open pores are formed. Each additional sphere removes one open pore and adds three giving a net increase of two. Hence total number of open pores $= 2\,(N - 3) + 2 = 2\,N—4$.

Since $N = \frac{r_0^3}{r^3}$, where $r_0^3 = \frac{3M}{4\pi\rho}$

Total number of open pores $= \frac{2r_0^3}{r^3} - 4$

Total open pore volume

$$V_p = 2\left(\sqrt{3} - \frac{\pi}{3} + \frac{1}{2}\cos^{-1}\frac{1}{3}\right)(r_0^3 - 2r^3)$$

putting $B = 2\left(\sqrt{3} - \frac{\pi}{3} + \frac{1}{2}\cos^{-1}\frac{1}{3}\right)$

$$V_p = B\,(r_0^3 - 2r^3)$$

Total Cavity Volume

The calculation of the volume of a cavity and the relation between the total cavity volume and the particle radius have been indicated in the previous paper.[1]

Total cavity volume

$$V_c = \left\{\frac{2\sqrt{2}}{3} - 4\left(\cos^{-1}\frac{1}{3} - \frac{\pi}{3}\right)\right\}(r_0^3 - 3r^3), \text{ or}$$

$$V_c = A\,(r_0^3 - 3r^3)$$

Total Capillary Volume

The total capillary volume V is made up of total cavity volume V_c and open pore volume V_p.

Total capillary volume,

$$V = ar_0^3 - br^3.$$

In the above equation a and b are positive constants. It is obvious from the above expression that the total capillary volume decreases as particle radius r increases.

Open Pore Volume in Relation to Cavity Volume

The ratio of the total open pore volume to the total cavity volume is given by

$$\frac{V_p}{V_c} = \frac{\sqrt{3} - \frac{\pi}{3} + \frac{1}{2}\cos^{-1}\frac{1}{3}}{\frac{\sqrt{2}}{3} + \frac{2\pi}{3} - 2\cos^{-1}\frac{1}{3}} \cdot \frac{r_0^3 - 2r^3}{r_0^3 - 3r^3}$$

putting

$$K = \frac{\sqrt{3} - \frac{\pi}{3} + \frac{1}{2}\cos^{-1}\frac{1}{3}}{\frac{\sqrt{2}}{3} + \frac{2\pi}{3} - 2\cos^{-1}\frac{1}{3}}$$

$$\frac{V_p}{V_c} = K\frac{r_0^3 - 2r^3}{r_0^3 - 3r^3}$$

If r tends to zero, $\frac{V_p}{V_c} \to K$.

As particle size diminishes, *i.e.*, as r tends to zero the ratio of the total open pore volume to the total cavity volume tends to the limiting value K.

If r tends to $\frac{r_0}{\sqrt[3]{4}}$, $\frac{V_p}{V_c} \rightarrow 2\,K$.

As particle size increases, the ratio increases until when the coalescence has proceeded so far that the whole mass consists of only four spherical particles producing a single cavity and four open pores, the ratio becomes 2 K. This represents the upper limit of the ratio since beyond this stage there can be no cavity.

Calculation of the cavity volume, open pore volume and hence the total capillary volume in relation to particle radius is made assuming a close packing of spherical particles of equiradius. This is not strictly true to random distribution. As remarked in the previous paper (*loc. cit.*), by the substitution of a suitable average value for r the form of the methematical formulation remains the same and the nature of the relation will not alter. The present mathematical approach of the problem is to be considered as a preliminary to a more rigorous quantitative formulation.

Summary

In a system of closely packed spherical particles, formation of two different types of capillaries—cavities and open pores—is indicated.

Assuming spherical particles of equiradius, the volume of an open pore is calculated in relation to particle radius. The total open pore is calculated in relation to particle radius. The total open pore volume just as the total cavity volume, decreases as the particle radius increases.

The ratio of the open pore volume to the cavity volume increases as particle radius increases. The value of this ratio when the particle radius is increased to the maximum limit at which the whole mass consists of four spheres producing a cavity and four open pores is twice the value when the particle radius tends to the limiting value of zero.

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NORMAL CO-ORDINATES OF SYMMETRIC POINT GROUPS*

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Introduction

A complete analysis of the normal modes of oscillation of a molecule is of great help in interpreting the Raman and infra-red absorption spectra. Brester,[1] Dennision[2] and others studied the normal modes of some symmetrical systems by employing special methods. For complicated cases, Wigner[3] had shown that the application of group theory greatly simplifies the work. Subsequently Tisza,[4] Wilson,[5] Placzek,[6] Rosenthal and Murphy[7] employed group theoretical methods and made important contributions to the subject. With the help of the theory of groups, we arrive at a set of co-ordinates called the symmetry co-ordinates which belong to different irreducible representations of the point group of symmetry operations of the system of particles constituting the molecule. The energy functions can be separately written in terms of the symmetry co-ordinates that belong to each irreducible representation. Further in the case of symmetry co-ordinates that belong to irreducible representations of dimension greater than unity, we need form the energy functions with respect to any one set of symmetry co-ordinates which belong to any particular row of matrices in the irreducible representation. The original secular equation obtained from the cartesian co-ordinates will be split up into the product of smaller secular equations when we use symmetry co-ordinates. By assuming a suitable force system, the actual normal co-ordinates can be derived from these symmetry co-ordinates. The normal co-ordinates that belong to the irreducible representations of dimension one are non-degenerate and the others are degenerate. The construction of non-degenerate normal co-ordinates is straight-forward but the construction of the degenerate normal co-ordinates is somewhat laborious. This difficulty of obtaining the degnerate normal co-ordinates is intimately connected with the problem of the determination of the actual irreducible representations of the point groups. The aim of the present paper is to give an alternative method by which the degenerate normal co-ordinates can be obtained with as much facility as the non-degenerate ones.

* One of the papers submitted for the Ramanujam Memorial Prize, 1941.

Normal Co-ordinates

To obtain the non-degenerate co-ordinates belonging to an irreducible representation of dimension unity, we start with the most general expression Q for the normal co-ordinate in terms of the $3n$ cartesian co-ordinates which specify the configuration of the n particles. If R is a symmetry operation of the point group

$$\mathbf{R}\,Q = \lambda Q, \tag{1}$$

where λ is the character of R in the irreducible representation. We get one such relation corresponding to each operation of the point group, but all these relations will not in general be independent. If there are n normal frequencies that belong to the irreducible representation, there will be left only n arbitrary constants in the general expression we have taken for Q in order that it may satisfy the character relations (1). From this expression for Q we form any n independent and mutually orthogonal functions which individually satisfy the character relations (1). One such choice is obviously to take the several terms in Q having the same arbitrary constant as so many independent functions. But whenever a translation or a rotation belongs to the irreducible representation, it is convenient to take the corresponding normal co-ordinate as one of the n functions and the other $n-1$ functions are chosen so that all the n functions together are independent and mutually orthogonal. A set of n such functions are called symmetry co-ordinates. Normal co-ordinates are then obtained by forming the kinetic and potential energy functions in terms of the symmetry co-ordinates and reducing both of them simultaneously to canonical forms.

For the construction of the degenerate symmetry co-ordinates by the above process we require the actual irreducible representations of the point groups. If $|\,a_{ij}\,|$ is the matrix corresponding to the operation R in the irreducible representation of dimension f, we take f general expressions $Q_1, Q_2 \ldots\ldots Q_f$ in the cartesian co-ordinates and use the equations of transformation

$$\mathbf{R}\,Q_i = \Sigma a_{ik}\,Q_k. \tag{2}$$

As before, if n is the number of frequencies that belong to the irreducible representation each of these general expressions contains n arbitrary constants in order that they may satisfy the above equations of transformation. We then form n sets of mutually orthogonal symmetry co-ordinates as before, each set containing the same number f of symmetry co-ordinates.

The determination of the actual irreducible representations of abstract groups is one of the difficult problems in the theory of groups. Unless we know the actual irreducible representations of the symmetry groups, the

previous method cannot be systematically applied for obtaining the normal co-ordinates. In a subsequent paper we derive the irreducible representations of the cubic point groups. The above method can be applied to determine the normal co-ordinates of any point system belonging to these groups. For all other groups we will describe below how we can obtain the degenerate normal co-ordinates by a method which is quite analogous to the non-degenarate case and which does not require the determination of the actual irreducible representations of the point groups.

Character Tables of the Point Groups

From the abstract group theoretical point of view, the 32 symmetry point groups may be divided into two classes. The first class consisting of groups G of the form $P^n = E$, $Q^2 = E$ and $PQ = Q P^{-1}$ and also $G \times H$ (the direct product of G and another group H of order 2) and the second class consisting of all the cubic groups. In this paper we consider point groups of the first class only.

The character tables of the dihedral groups G can be built from the characters of the cyclic group G_1 which is generated by the operation P. As the operations of G_1 are all commutative, each element is a conjugate class by itself and therefore there are n irreducible representations for G_1 and all of them are easily seen to be one-dimensional and they can be represented by the n correspondences

$$P \sim \omega_r \quad (r = 1, 2, \ldots\ldots n)$$

where ω_r is one of the nth roots of unity.

In the case of the dihedral groups there are two cases to be considered. Case (1) is that in which n is odd. The conjugate classes of elements in this case are

$$E\ ;\ (P,\ P^{n-1})\ ;\ (P^2,\ P^{n-2}) \ldots . (P^{n-1},\ P^{n+1});\ \text{and}\ (Q,\ QP,\ QP^2 \ldots . QP^{n-1}).$$

Thus there are $\frac{n+3}{2}$ irreducible representations for this group. Now the only representation of $2n$, the order of the group, as the sum of squares of $\frac{n+3}{2}$ integers is

$$2n = 1^2 + 1^2 + \left(\frac{n-1}{2}\right) 2^2$$

and therefore for this group there are two one-dimensional and $\frac{n-1}{2}$ two-dimensional representations. The two one-dimensional representations are

$$P \sim 1 \text{ and } Q \sim 1 \text{ or } -1.$$

Since Q is of order two and it is not commutative with P, its representation in the two-dimensional irreducible representations must be the matrix

$$\begin{vmatrix} 0 & -1 \\ 1 & 0 \end{vmatrix}$$

or one of its conjugates and therefore its character is 0 in all the two-dimensional irreducible representations. To determine the characters of the elements of the cyclic group G_1 in the point group G, it may be noted that the matrices corresponding to the elements of G_1 in the irreducible representations of G define a representation of G_1 but not necessarily irreducible. Since the irreducible representations of G_1 are all one-dimensional it follows that every two-dimensional irreducible representation of G splits up into two one dimensional irreducible representations of G_1. The elements P^s and P^{-s} have the same character, as they belong to the same conjugate class, in the several irreducible representations of G and they have complex conjugate and therefore different characters in the irreducible representations of G_1. Therefore the two complex conjugate characters of the cyclic group G_1 give rise to the character relation

$$P^s \sim 2 \cos s\omega_r$$

in the irreducible representation E_r of the dihedral group G. The character table for the entire group G is thus completed and the character table is

	P^s	Q
A_1	1	1
A_2	1	-1
E_r	$2 \cos sr\omega$	0

$$\left(s = 0, 1, 2 \ldots . n;\ r = 1, 2, \ldots \ldots \frac{n-1}{2}\right)$$

where ω is one of the primitive nth roots of unity. Case (2) is that in which n is even. A similar argument shows that there are four one dimensional and $\frac{n-2}{2}$ two-dimensional irreducible representations and the character table is

	P^s	Q
A_1	1	1
A_2	1	-1
B_1	$(-1)^s$	1
B_2	$(-1)^s$	-1
E_r	$2 \cos sr\omega$	0

$$\left(s = 0, 1, 2 \ldots \ldots n;\ r = 1, 2 \ldots \ldots \frac{n-2}{2}\right)$$

Since G × H is the direct product of G and H, the characters of the conjugate classes of G × H are the products of the corresponding characters of the conjugate classes of G and H.

The Degenerate Normal Co-ordinates

The following result can now be easily proved. If $X + iY$ is the symmetry co-ordinate that belongs to the irreducible representation E′ of G_1 then X, Y is a pair of degenerate symmetry co-ordinates belonging to the irreducible representation E of G. To prove this if $R = P^s$ is an operation in G_1

$$\overline{R}\,(X + iY) = (\cos sr\,\omega + i \sin sr\,\omega)\,(X + iY)$$

in the rth irreducible representation of the cyclic group. Equating the real and imaginary parts we have

$$\overline{R}\,X = \cos sr\,\omega\,X - \sin sr\,\omega\,Y$$
$$\overline{R}\,Y = \sin sr\,\omega\,X + \cos sr\,\omega\,Y$$

and therefore the character of R defined by X and Y is $2 \cos sr\,\omega$. Similarly the character arising from P^{-s} is also equal to $2 \cos sr\,\omega$. This shows that X, Y form a set of symmetry co-ordinates which belong to the irreducible representation E of the point group G.

In order therefore to obtain the degenerate symmetry co-ordinates of a point group G, we take the cyclic group generated by the basis operation P which is either a rotation or a rotation-reflection about a symmetry axis and obtain the complex non-degenerate symmetry co-ordinates belonging to the irreducible representations of the cyclic group. The real and imaginary parts of each of these symmetry co-ordinates taken separately constitute a pair of symmetry degenerate co-ordinates of the original point group. In the case of the groups G × H, the co-efficients in the expression $X + iY$ obtained from G_1 should be so chosen that it is either symmetric or anti-symmetric with respect to the basis operation in H. The degenerate symmetry co-ordinates are then found as before.

My grateful thanks are due to Prof. S. Bhagavantam for the constant help and encouragement he has been giving me.

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RAMAN EFFECT AND HYDROGEN BONDS

Part VIII. A Note on the Solutions of Coumarin in Mineral Acids

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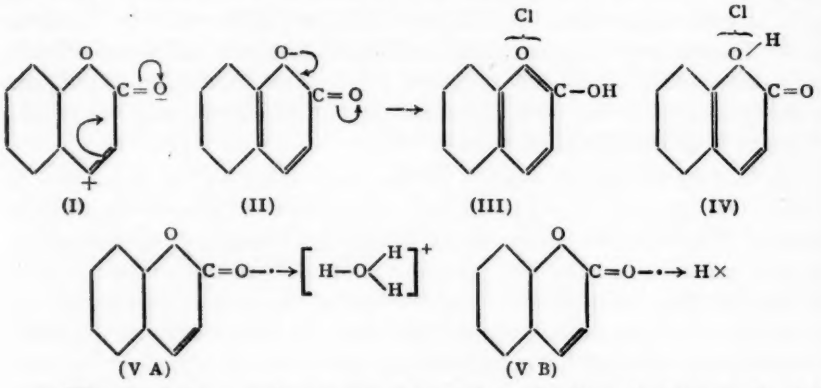
Among carbonyl compounds coumarin is unique in that it forms "True Hydrogen Bonds[1]" with all acceptor solvents so far studied, phenol, chloroform, methyl and ethyl alcohols and acetic acid. Irrespective of the concentrations of the solutions and the capacities of the solvent molecules to form hydrogen bonds, the whole of the coumarin present enters into combination, so that in the Raman spectrum of the solutions the original carbonyl frequency of coumarin disappears completely and a modified frequency alone is present.[2,3] In almost all other cases of carbonyl compounds the association between solute and solvent molecules is not complete and consequently both the original and modified C = O frequencies are noticed.

Though coumarin is sparingly soluble in water, considerable amount of it goes into solution in concentrated mineral acids. It dissolves up to 5% easily in cold concentrated hydrochloric acid and more of it is dissolved by the fuming acid. Concentrated nitric and sulphuric acids can dissolve much larger quantities of the solid, and solutions containing up to 50% can be easily made in the cold. On diluting the solutions with water the substance is precipitated unchanged.

In looking for an explanation of the high solubility of coumarin in aqueous mineral acids it is obvious that some kind of loose combination is involved. If an additive reaction be considered as a possibility, the capacity of the acid molecules to enter into such a reaction is dependent on the nature of the ions that they can produce. Of the two ions of the mineral acids mentioned above, the anions are more stable and the reactivity is dependent on the kationoid reactivity (electrophilic nature) of hydrogen ions. In regard to the coumarin molecule the following three centres of reactivity have to be considered : (1) the carbonyl group (C = O), (2) the ethylenic double bond (C = C) and (3) the pyrone oxygen. With reference to addition reactions, (1) is always kationoid (electrophilic), the reaction being initiated at the C atom and (2) also becomes kationoid in reactivity due to the existence of electromeric polarisation as shown in formula (I) below. Consequently these two centres of reactivity cannot be affected by the electrophilic acid reagents. Further,

the looseness of the combination involved definitely shows that addition at these centres does not take place, since additive compounds produced from ethylenic and carbonyl groups should be more stable. Regarding additive properties of (3), the pyrone oxygen, in forming oxonium salts all evidence seems to support the opinion that the oxygen and the C = O group work in conjunction (see formula II) to form a hydroxypyrylium salt as shown in (III) and not a pyronium compound of type (IV). Though an oxygen atom in ether may be capable of forming oxonium salts directly, when it exists in conjugation with a carbonyl group, the two seem to function together. In this connection may be mentioned the high Raman frequency of the C = O group in esters and particularly in the phenyl esters, as compared with the other types of compounds having the carbonyl group. This has been explained by us as due to the existence of polarisation similar to (II).[4]

There is a further possible mode of combination between coumarin and the mineral acids through the formation of hydrogen bonds as represented by formula (V). The question whether this happens or a hydroxy pyrylium salt is formed, can be solved by a study of the Raman spectrum of the solutions of coumarin in mineral acids. If structure (III) is formed the carbonyl frequency of coumarin should disappear, and if (V) is formed the frequency should undergo change, but should exist in the C = O region.



[The symbol —·→ is now proposed to indicate a hydrogen bond in order to distinguish it from a co-ordinate bond which is ordinarily represented by an unbroken arrow.]

Details regarding the Raman spectrum of coumarin in the solid state and in solutions in various solvents have already been given.[5] The carbonyl frequency of the solution in a non-polar solvent, carbon tetrachloride (1742 cm.$^{-1}$) is taken as the standard for comparison. The pure substance

is dissolved in concentrated hydrochloric acid in the cold and a clear solution is obtained by rapidly filtering off the excess of the solid through a sintered glass funnel. A 5% solution could thus be made and employed for investigation. Though there is a good amount of continuous spectrum, the C = C and C = O regions are clear. It is noticed that the ethylenic frequencies are unaffected and are the same as those found in the spectrum of coumarin in carbon tetrachloride. There is a prominent C = O frequency, but it has undergone a shift from 1742 to 1720 cm.$^{-1}$ and is rather diffuse. As in other solutions of this substance the original C = O frequency has completely disappeared and a new one has taken its place. It could therefore be concluded that a hydroxypyrylium salt of type (III) is not formed and that the enhanced solubility of coumarin in hydrochloric acid is due to the formation of hydrogen bond as in (V).

A saturated solution of coumarin in cold concentrated nitric acid is coloured pale yellow. But a solution containing about 20–25% of coumarin is suitable for the study of the Raman spectrum and can be easily made. Almost the same results are obtained as in the case of the hydrochloric acid solution. The ethylenic frequencies are unchanged and the modified C = O frequency is at 1722 cm.$^{-1}$ The existence of complexes of type (V) involving hydrogen bonds is established in this case also.

With the concentrations of the acids employed, 33% hydrochloric acid and 68% nitric acid which approximate to 10 N, there does not seem to exist unequivocal evidence for complete ionisation. It is therefore difficult to say definitely whether structure (VA) involving hydrated hydrogen ions or (VB) involving undissociated molecules of the acids represents the correct nature of the complexes involved.

Solutions of coumarin in concentrated sulphuric acid did not give clear pictures due to the existence of continuous spectrum and some fluorescence.

Summary

The marked solubility of coumarin in aqueous mineral acids is attributed to the formation of complexes. That this takes place through hydrogen bonds is shown by a study of the Raman spectrum of these solutions wherein the carbonyl frequency is found to be considerably lowered, but still persists.

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LATTICE POINTS IN A RIGHT-ANGLED TRIANGLE—II

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Let L (N) denote the number of lattice points in the right-angled triangle bounded by the axes and the line $x\omega + y\omega' = N$, including those on the axes. In a paper,[1] published in 1922, Hardy and Littlewood have considered this problem. In this paper, I deal with this problem by a different method. As a matter of fact, L (N) is expressed in terms of S (θ, N), where

$$S(\theta, N) = \sum_{n=1}^{N} \{\theta n\}, \quad \{x\} = x - [x] - \tfrac{1}{2}, \tag{1}$$

and $\theta = \omega/\omega'$ is irrational. (2)

S (θ, N) was considered by me in a paper with the same title.[2]

Further, the following notations are used.

$$F(N) = \frac{(N+\omega)(N+\omega')}{2\omega\omega'}; \quad \Delta(N) = L(N) - F(N) \tag{3}$$

If $\frac{p_r}{q_r}$ be the rth convergent for θ, when

$$\theta = a_1 + \frac{1}{a_2} + \frac{1}{a_3} + \ldots\ldots, \quad q_{r-1} < N \leqslant q_r,$$

$$\sigma(N) = a_1 + a_1 + \ldots\ldots + a_r. \tag{4}$$

§ 2. Lemma (1): $L(a) = 1 + \left[\frac{a}{\omega}\right] + \sum_{r=0}^{a/\omega} \left[\frac{a}{\omega'} - r\theta\right]$.

We have to solve $x\omega + y\omega' \leqslant a$, $x \geqslant 0$, $y \geqslant 0$.

If x is fixed, the number of values for $y = 1 + \left[\frac{a}{\omega'} - x\theta\right]$.

But x takes $\left[\frac{a}{\omega}\right] + 1$ values from 0 to $\left[\frac{a}{\omega}\right]$.

Hence the lemma is proved.

Lemma (2): $\Delta(a) - \Delta(a-\omega) = -\left\{\frac{a}{\omega'}\right\}$.

From (3) and lemma (1),

$$\Delta(a)-\Delta(a-\omega)=\mathrm{L}(a)-\mathrm{L}(a-\omega)-\mathrm{F}(a)+\mathrm{F}(a-\omega)$$

$$=1+\left[\frac{a}{\omega}\right]+\sum_{r\leqslant a/\omega}\left[\frac{a-r\omega}{\omega'}\right]-1-\left[\frac{a-\omega}{\omega'}\right]-\sum_{r}\left[\frac{a-\omega-r\omega}{\omega'}\right]$$

$$-\frac{1}{2\omega\omega'}\Big((a+\omega)\ (a+\omega')-a\,(a-\omega+\omega')\Big)$$

$$=1+\left[\frac{a}{\omega'}\right]-\frac{1}{2\,\omega\omega'}\ (a\omega+\omega\omega'+a\omega)=\left[\frac{a}{\omega'}\right]-\frac{a}{\omega'}+\frac{1}{2}=-\left\{\frac{a}{\omega'}\right\}.$$

LEMMA (3): $\Delta(n\omega)=\frac{1}{2}-\mathrm{S}(\theta,\ n)$.

From Lemma (2), $\Delta(n\omega)-\Delta(\overline{n-1}\omega)=-\left\{\frac{n\omega}{\omega'}\right\}=-\{n\theta\}$.

$$\Delta(\overline{n-1}\omega)-\Delta(\overline{n-2}\omega)=-\{(n-1)\theta\}$$

. . . . . .

. . . . . .

$$\Delta(2\omega)-\Delta(\omega)=-\{2\theta\}$$

$$\Delta(\omega)=\mathrm{L}(\omega)-\mathrm{F}(\omega)=2+[\theta]-\frac{1}{\omega'}\ (\omega+\omega')$$

$$=\tfrac{1}{2}-\{\theta\}.$$

Adding, we get the lemma.

§ 3. THEOREM I: If m, n are integers,

$$\Delta(n\omega+m\omega')=\Delta(n\omega)+\Delta(m\omega')-\tfrac{1}{2}.$$

From lemma (2),

$$\Delta\ (n\omega+m\omega')-\Delta(\overline{n-1}\ \omega+m\omega')=-\left\{\frac{n\omega+m\omega'}{\omega'}\right\}=-\left\{\frac{n\omega}{\omega'}\right\}$$

$$=-\{n\theta\}.$$

. . . . . .

. . . . . .

$$\Delta\ (\omega+m\omega')-\Delta\ (m\omega')\qquad=-\{\theta\}.$$

Adding, $\Delta(m\omega+n\omega')=\Delta(m\omega')-\mathrm{S}(\theta,\ n)$.

From this and lemma (3), we get the theorem.

LEMMA (5): If $m=[n\theta]$,

$$\mathrm{L}(n\omega+m\omega')=(n+1)\ (m+1)+nm.$$

Proof is exactly similar to Theorem 7 in a previous paper of mine.[3]

THEOREM II: If $m=[n\theta]=n\theta-\phi$, then $\Delta(n\omega+m\omega')=\frac{1}{2}(1-\phi)\left(\frac{1+\phi}{\theta}\right)$.

Proof is similar to that of Theorem 8 in the paper mentioned abov.

§ 4. If $m=[n\theta]$, from Theorem II, $\Delta(n\omega+m\omega')=0(1)$.

So from Theorem I, when $m=[n\theta]$,

$$\Delta(m\omega')=\Delta(n\omega+m\omega')-\Delta(n\omega)+0(1)=-\Delta(n\omega)+0(1)$$
$$=S(\theta, n)+0(1), \text{ from lemma (3).}$$

Further $\Delta(n\omega)=-S(\theta, n)+0(1)$.

So we get

THEOREM III: Whether $S(\theta, n)$ is bound on one side or not, $\Delta(X)$ becomes positively and negatively equally large.

Since[2] $|S(\theta, n)|>k\log n$ for an infinity of values of n, we get

THEOREM IV: $\Delta(N)>k\log N$ and $\Delta(M)<-k\log M$ for infinity of values of N and M.

Hardy and Littlewood prove only that

$|\Delta(N)|>k\log N$ for infinitely many values of N.

§ 5. Let $A_1, A_2, A_3, \ldots$ denote the numbers $n\omega+m\omega'$ in increasing order, $h=A_{r+1}-A_r$, and $N=A_{r+1}$.

Since[2] $S(\theta, n)=0(\sigma(n))$, from Theorem I, II,

$$\Delta(N)=\Delta(A_{r+1})=\Delta(n\omega)+\Delta(m\omega')+0(1)$$
$$=\Delta(n\omega)-\Delta(n_1\omega)+0(1), \text{ where } m=[n_1\ \theta],$$
$$=-S(\theta, n)+S(\theta, n_1)+0(1)$$
$$=0(\sigma(n)+\sigma(n_1))=0(\sigma(N)). \tag{5}$$

Again, $\Delta(N)=\Delta(A_{r+1})=L(A_{r+1})-F(A_{r+1})$

$$=1+L(A_r)-F(A_r)-F(A_{r+1})+F(A_r)$$
$$=1+\Delta(A_r)-(F(A_{r+1})-F(A_r))$$
$$=0(\sigma(N)-(F(A_r+h)-F(A_r)), \text{ from (5),}$$
$$=0(\sigma(N))-\frac{1}{2\omega\omega'}((A_r+h+\omega)(A_r+h+\omega')-(A_r+\omega)(A_r+\omega'))$$
$$=0(\sigma(N))-\frac{1}{2\omega\omega'}(h(2A_r+\omega+\omega'+h))$$
$$=-\frac{A_r h}{\omega\omega'}+0(\sigma(N)), \text{ because } h=0(1).$$

So $\frac{A_r h}{\omega\omega'}=0(\sigma(N))$; for $\Delta(N)=0(\sigma(N))$,

so that $h=0\left(\frac{\sigma(N)}{N}\right)$.

Hence we get

THEOREM V: $A_{r+1} - A_r = 0\left(\frac{\sigma(A_r)}{A_r}\right)$.

THEOREM VI: $\Delta(n) = 0(\sigma(n))$.

Let $A_r \leqslant n < A_{r+1}$.

$\Delta(n) = L(n) - F(n) = L(A_r) - F(A_r) - (F(n) - F(A_r))$

$= \Delta(A_r) + 0(F(A_r + h) - F(A_r))$, where $h = A_{r+1} - A_r$,

$= \Delta(A_r) + 0(A_r \cdot h) = 0(\sigma(n))$, from (5) and Theorem V.

§ 6. THEOREM VII: If ω, ω', N are any three positive real numbers, and $\theta = \frac{\omega}{\omega'}$ is irrational, we can find positive integers n, m such that

$$N - n\omega - m\omega' = 0\left(\frac{\sigma(N)}{N}\right),$$

and in particular

$$N - n\omega - m\omega' \to 0 \text{ as } N \to \infty.$$

We can find r such that

$$A_r \leqslant N < A_{r+1}.$$

Let $A_r = n\omega + m\omega'$.

Then $N - n\omega - m\omega' = N - A_r \leqslant A_{r+1} - A_r = 0\left(\frac{\sigma(N)}{N}\right)$ from Theorem V.

Since $\sigma(N) = o(N)$, the second part follows from this.

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LATTICE POINTS IN A RIGHT-ANGLED TRIANGLE—III

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§ 1. Let $N(\eta)$ denote the number of lattice points in the right-angled triangle bounded by the axes and the line

$$ax+by=\eta,$$

including those on the sides, where

a and b are co-prime positive integers. (1)

$\theta=\eta-[\eta]$, where $[x]$ denotes the integral part of x. (2)

$$P(\eta)=\frac{1}{2ab}\{(\eta+a)(\eta+b)+\eta(1-2\theta)\}. \tag{3}$$

$$E(\eta)=N(\eta)-P(\eta). \tag{4}$$

Then, in his latest book 'Ramanujan', Hardy proves, by the method of contour integration, that

$$E(\eta)=O(1).$$

In the above we cannot say that the constant in O is independent of a, b, and it may require further consideration to derive the relation.

In this paper, I prove, by an easy elementary method, that $E(\eta)=O(a+b)$, where the constant in O is independent of a, b.

Hereafter, the constant in O is independent of a, b. (5)

Further let $M(r)$ denote the number of integral solutions of

$$ax+by=r; \tag{6}$$

and $$\eta=n+\theta=mab+t+\theta, \text{ where } n=[\eta],\ 0\leqslant t<ab. \tag{7}$$

§ 2. Lemma (1): $M(r)=\left[\frac{r}{ab}\right]+1$ or $\left[\frac{r}{ab}\right]$ according as $a\beta+b\alpha=t$, (with $0\leqslant\alpha<a$, $0\leqslant\beta<b$), is solvable or not, where $r=kab+t$, $0\leqslant t<ab$.

This is proved in the foot-note on p. 71 of Hardy's book mentioned above.

LEMMA (2): If k denotes the number of solutions of $a\beta + b\alpha < ab$, $0 \leqslant \alpha < a$, $0 \leqslant \beta < b$, then

$$k = \frac{(a+1)\,(b+1)}{2} - 1.$$

When $\alpha = 0$, $a\beta < ab$; so the number of values of $\beta = b$.

When $1 \leqslant \alpha \leqslant a-1$, $\beta < \frac{ab - b\alpha}{a}$; so the number of values of $\beta = \left[\frac{b\,(a-\alpha)}{a}\right] + 1$.

Hence $k = b + \sum_{\alpha=1}^{a-1} \left\{\left[\frac{b\,(a-\alpha)}{a}\right] + 1\right\} = b + a - 1 + \sum_{r=1}^{a-1} \left[\frac{rb}{a}\right]$

$$= a + b - 1 + \sum_{r=1}^{a-1} \frac{rb}{a} - \frac{1}{a}\,(1 + 2 + \ldots + a - 1)$$

$$= a + b - 1 + \frac{b\,(a-1)}{2} - \frac{a-1}{2} = \frac{(a+1)\,(b+1)}{2} - 1.$$

LEMMA (3): When $0 \leqslant t < ab$, $\mathrm{N}(t) = \frac{t^2}{2ab} + \mathrm{O}(a+b)$.

Now $\mathrm{N}(t)$ is equal to the number of solutions of

$$a\beta + b\alpha \leqslant t;\quad 0 \leqslant \alpha < a;\quad 0 \leqslant \beta < b.$$

But $$\beta = \left[\frac{t - b\alpha}{a}\right] + 1,\ \alpha = 0, 1, \ldots, \left[\frac{t}{b}\right].$$

Let $$\phi = \frac{t}{b} - \left[\frac{t}{b}\right], \text{ and } \phi_\alpha = \frac{t - b\alpha}{a} - \left[\frac{t - b\alpha}{a}\right].$$

Then $$\mathrm{N}(t) = \sum_\alpha \left\{\left[\frac{t - b\alpha}{a}\right] + 1\right\} = \left[\frac{t}{b}\right] + 1 + \sum_\alpha \left\{\frac{t - b\alpha}{a} - \phi_\alpha\right\}$$

$$= \frac{t}{b} + 1 - \phi + \frac{t}{a}\left(\frac{t}{b} + 1 - \phi\right) - \frac{b}{2a}\left(\frac{t}{b} - \phi\right)\left(\frac{t}{b} - \phi + 1\right) - \Sigma\,\phi_\alpha$$

$$= \frac{t^2}{2ab} + \frac{t}{2a} + \frac{t}{2b} + \frac{1}{2} + \frac{t}{2b} - \Sigma\,\phi_\alpha - \phi + \frac{1}{2} + \frac{b}{2a}\,\phi\,(1 - \phi). \qquad (8)$$

Since $t < ab$, $\frac{t}{2a} = \mathrm{O}(b)$, $\frac{t}{2b} = \mathrm{O}(a)$, $\Sigma\,\phi_\alpha = \mathrm{O}\left(\frac{t}{b}\right) = \mathrm{O}(a)$.

Hence $\mathrm{N}(t) = \frac{(t+a)\,(t+b)}{2ab} + \mathrm{O}(a+b) = \frac{t^2}{2ab} + \mathrm{O}(a+b)$.

LEMMA (4): If $\mathrm{A}(r+1) = \mathrm{N}\{(r+1)\,ab - 1\} - \mathrm{N}\{rab - 1\}$,

then $$\mathrm{A}(r+1) = rab + k.$$

Now $A(r+1) = \Sigma M(n)$ when n runs from rab to $(r+1)\,ab - 1$, (both inclusive).

So $$A(r+1) = \sum_{t=0}^{ab-1} M(rab+t)$$

$$= \sum_{t=0}^{ab-1} \left[\frac{rab+t}{ab}\right] = N(ab-1), \text{ {from lemma (1)},}$$

$$= \sum_{t} r + k, \text{ {from lemma (2)}}$$

$$= rab + k.$$

§ 3. THEOREM I: $N(\eta) = P(\eta) + O(a+b)$.

Now $N(\eta) = N(n) = N(mab+t)$

$$= \sum_{r=0}^{m-1} \{N((r+1)\,ab - 1) - N(rab-1)\} + N(mab+t) - N(mab-1)$$

$$= \sum_{r=0}^{m-1} (rab+k) + \sum_{r=0}^{t} M(mab+r), \text{ from lemma (4),}$$

$$= mk + \frac{1}{2}\,abm(m-1) + \sum_{r=0}^{t} \left[\frac{mab+r}{ab}\right] + N(t), \text{ from lemma (1),}$$

$$= mk + \frac{1}{2}\,abm(m-1) + m(t+1) + \frac{t^2}{2ab} + O(a+b), \text{from lemma (3),}$$

$$= \frac{1}{2}\,mab + \frac{1}{2}\,ma + \frac{1}{2}\,mb - \frac{1}{2}\,m + \frac{1}{2}\,m^2ab - \frac{1}{2}\,mab$$

$$+ mt + m + \frac{t^2}{2ab} + O(a+b), \text{ (by substituting for } k).$$

$$= \frac{1}{2ab}\left\{a^2b^2m^2 + 2abmt + t^2\right\} + \frac{mab}{2b} + \frac{mab}{2a} + \frac{mab}{2ab} + O(a+b)$$

$$= \frac{1}{2ab}(abm+t)^2 + \frac{n-t}{2b} + \frac{n-t}{2a} + \frac{n-t}{2ab} + O(a+b), \text{ from (7),}$$

$$= \frac{n^2}{2ab} + \frac{n}{2b} + \frac{n}{2a} + \frac{n}{2ab} + O(a+b)$$

$$= \frac{1}{2ab}\left\{(\eta-\theta)^2 + (\eta-\theta)(a+b+1)\right\} + O(a+b), \text{ from (7),}$$

$$= \frac{1}{2ab}\left\{\eta^2 + \eta a + \eta b + \eta - 2\eta\theta + O(a+b)\right\} + O(a+b)$$

$$= \frac{1}{2ab}\left\{(\eta+a)(\eta+b) + \eta(1-2\theta)\right\} + O(a+b).$$

§ 4. THEOREM II: $\mathrm{E}(\eta) = \Omega(a+b)$.

From (8), when $t < ab$,

$$\mathrm{E}(t) = \frac{t}{2b} - \Sigma\phi_\alpha + \mathrm{O}\left(1+\frac{b}{a}\right). \tag{9}$$

(1) Put $t = \frac{ab}{2}$ where $b = 1$ and a is even.

Then $\phi_\alpha = \frac{t-b\alpha}{a} - \left[\frac{t-b\alpha}{a}\right] = \frac{1}{2} - \frac{\alpha}{a}$ when $\alpha \leqslant \frac{a}{2}$.

So $\Sigma\,\phi_\alpha = \frac{a}{4} - \frac{1}{a}\left(1+2+\cdots+\frac{a}{2}\right) = \frac{a}{8} + \mathrm{O}(1)$.

Hence from (9), $\mathrm{E}(t) = \frac{a}{8} + \mathrm{O}(1)$. (10)

(2) Put $t = \frac{ab}{2}$ $b = a-1$, a is even.

Then $\frac{t-b\alpha}{\alpha} = \frac{a-1}{2} - \frac{(a-1)\alpha}{a} = \frac{a-1}{2} - a + \frac{\alpha}{a}$.

When $\alpha < \frac{a}{2}$, $\phi_\alpha = \frac{1}{2} + \frac{\alpha}{a}$.

So $\Sigma\phi_\alpha = \frac{a}{4} + \frac{a}{8} + \mathrm{O}(1) = \frac{3a}{8} + \mathrm{O}(1)$.

Hence $\mathrm{E}(t) = -\frac{a}{8} + \mathrm{O}(1)$. (11)

From (10) and (11), the theorem follows.

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